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(54) **Ink jet dye design**

(57) Magenta chromophore dyes which are stabilized by adding steric hindering groups to protect the imino carbons; nonlimiting examples of the steric hindering groups being phenyl, methyl, ethyl, isopropyl, fluoride, chloride, bromide and iodide groups.

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Description

FIELD OF THE INVENTION

5 [0001] The present invention generally relates to ink-jet printing, and in particular to a specific dye and ink sets for improving ink-jet print stability.

BACKGROUND OF THE INVENTION

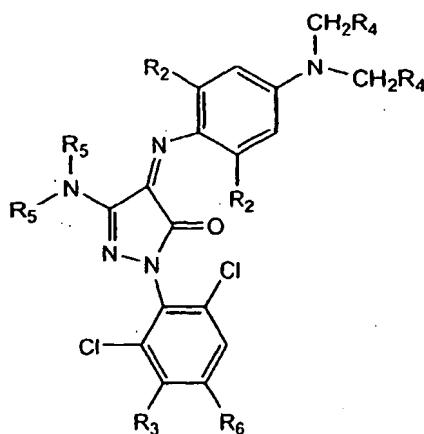
10 [0002] Ink-jet printing is a non-impact printing process in which droplets of ink are deposited on a print medium in a particular order to form alphanumeric characters, area-fills, and other patterns thereon. Low cost and high quality of the hardcopy output, combined with relatively noise-free operation, have made ink-jet printers a popular alternative to other types of printers used with computers. Notwithstanding their recent success, intensive research and development efforts continue toward improving ink-jet print quality. A surge in interest in ink-jet printing has resulted in the need to
15 produce high quality prints at a reasonable cost. The challenge remains to further improve the print quality and lightfastness of ink-jet prints. The emerging use of ink-jet prints for digital photos, requires high-resolution images that have accurate color and are durable.

[0003] Manufacturers of photographic film and print media have come up with dyes reported to have a display life of up to 60 years. A search of patents by Fuji revealed that they have developed a class of dyes, which when used in photographic media, are very stable. However, this class of dyes has been found not to be very stable toward light. Lightfastness is a very important quality in a dye used in ink-jet printing. Further, it is known that these azopyrazolone dyes can be attacked by ozone at the imine carbon. These shortcomings of such known photographic dyes, especially in the magenta and magenta-containing colors, make them unsuitable for use in ink-jet printing.

20 [0004] Accordingly, investigations continue into developing ink formulations which have improved properties and which do not improve one property at the expense of the others. Thus, there remains a need in the art to further improve the print quality, color gamut, and lightfastness of the ink-jet prints without sacrificing pen performance and reliability, particularly when trying to reproduce the color gamut of silver halide prints.

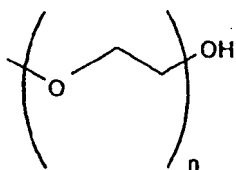
SUMMARY OF THE INVENTION

30 [0005] The present invention relates to a magenta ink for ink-jet printing, comprising a dye having a structure as follows:



R2 is selected from the group consisting of methyl, ethyl, propyl, isopropyl and halogen;

R3 is selected from the group consisting of H, SO₃H, COOH, and a polyether group



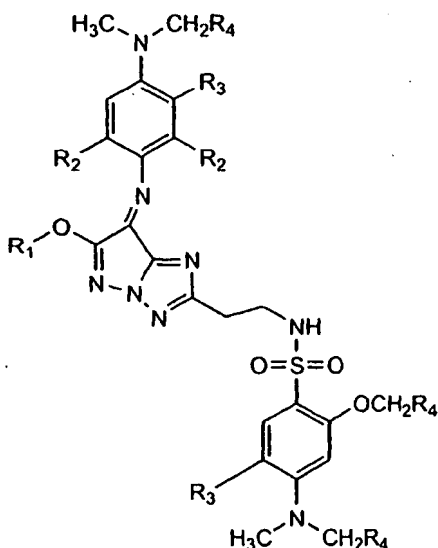
where n is from 2 to 100;

R4 is selected from the group consisting of H, SO₃H, COOH, CH₂SO₃H, CH₂COOH, C₂H₄SO₃H and C₂H₄COOH;

R5 is selected from the group consisting of ethyl, propyl, isopropyl, phenyl, substituted phenyl and R4; and

R6 is selected from the group consisting of H, halogen, methyl, amino, substituted amino, R4 and R3.

[0006] The present invention also relates to a magenta ink for ink-jet printing, comprising a dye having the following structure:

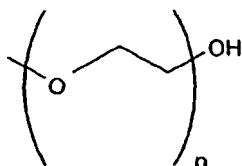


wherein

R1 is selected from the group consisting of ethyl isopropyl, isobutyl, phenyl and substituted phenyl;

R2 is selected from the group consisting of methyl, ethyl, propyl, isopropyl and halogen;

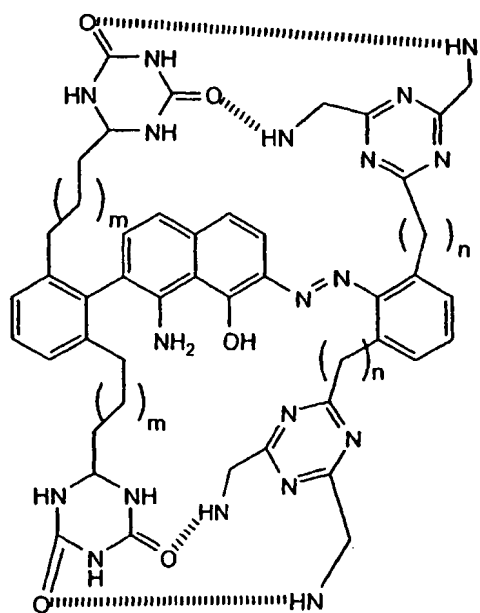
R3 is selected from the group consisting of H, SO₃H, COOH, and a polyether group



where n is from 2 to 100; and

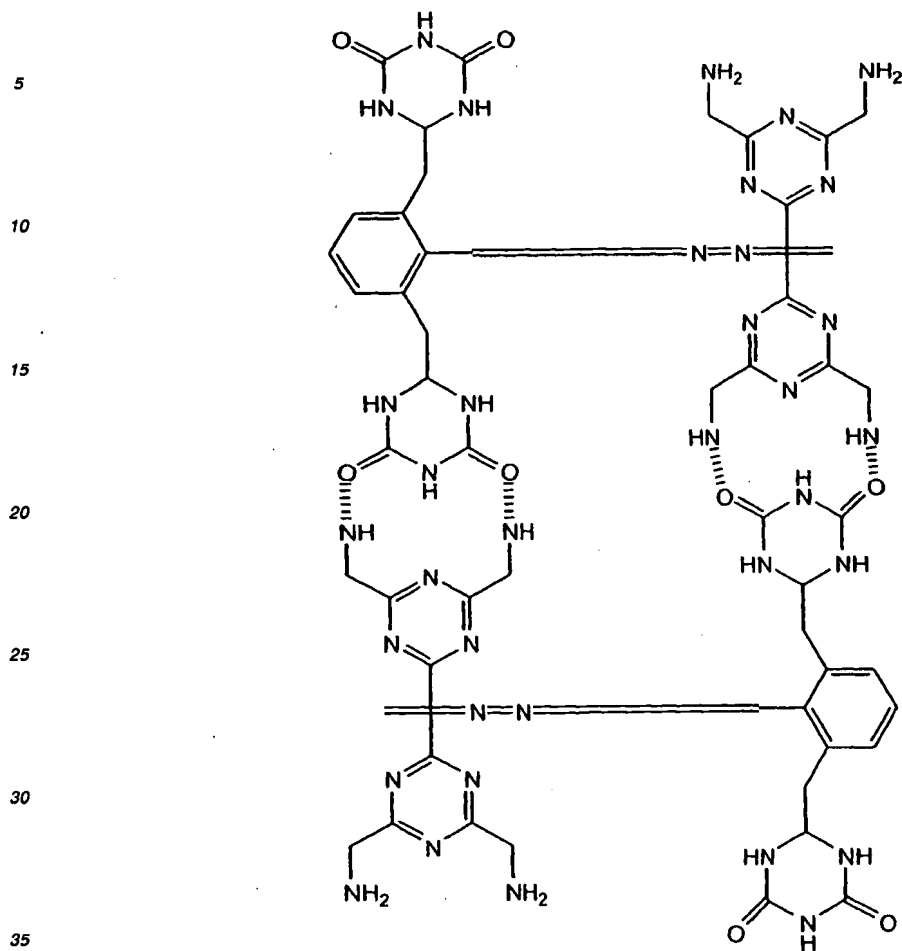
R4 is selected from the group consisting of H, SO₃H, COOH, CH₂SO₃H, CH₂COOH, C₂H₄SO₃H and C₂H₄COOH.

[0007] In addition the present invention relates to a magenta ink for ink-jet printing, comprising a dye having the following structure:



wherein m and n are from 0 to 4 added carbons.

[0008] Furthermore the present invention relates to a magenta ink for inkjet printing comprising a dye having the following structure:



wherein

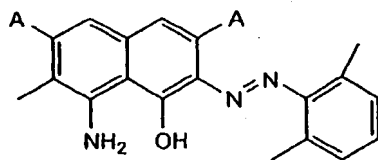
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is an azo dye structure

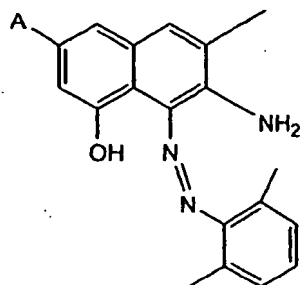
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wherein A is selected from H and SO₃H,
or a gamma acid based dye structure

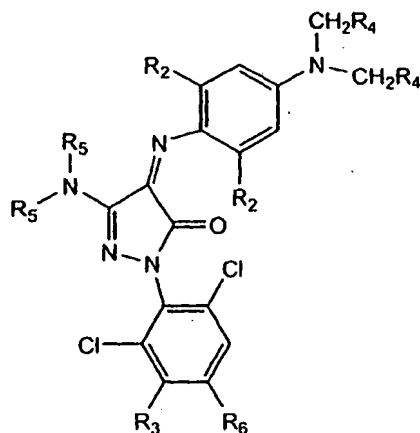
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wherein A is selected from H and SO₃H.

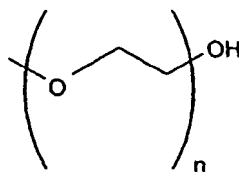
The present invention also relates to a method for ink-jet printing, comprising:

providing at least one magenta ink containing at least one magenta dye having a visible light absorbance of 0.01 to 0.57 at λ_{max} at a 1:10,000 dilution in water and having a structure as follows:



R2 is selected from the group consisting of methyl, ethyl, propyl, isopropyl and halogen;

R3 is selected from the group consisting of H, SO₃H, COOH, and a polyether group



where n is from 2 to 100;

R4 is selected from the group consisting of H, SO₃H, COOH, CH₂SO₃H, CH₂COOH, C₂H₄SO₃H and C₂H₄COOH;

R5 is selected from the group consisting of ethyl, propyl, isopropyl, phenyl, substituted phenyl, and R4; and

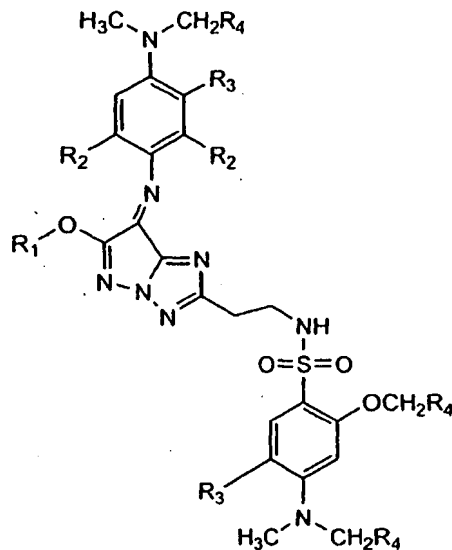
R6 is selected from the group consisting of H, halogen, methyl, amino, substituted amino, R4 and R3.

; and

printing said ink on a printing medium by means of an ink-jet pen.

[0009] In addition the present invention relates to a method for ink-jet printing, comprising:

providing at least one magenta ink containing at least one magenta dye having a visible light absorbance of 0.01 to 0.57 at λ_{\max} at a 1:10,000 dilution in water and having a structure as follows:

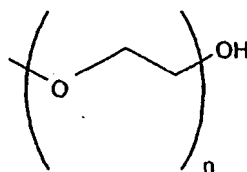


wherein

R1 is selected from the group consisting of ethyl isopropyl, isobutyl, phenyl and substituted phenyl;

R2 is selected from the group consisting of methyl, ethyl, propyl, isopropyl and halogen;

R3 is selected from the group consisting of H, SO₃H, COOH, and a polyether group



where n is from 2 to 100; and

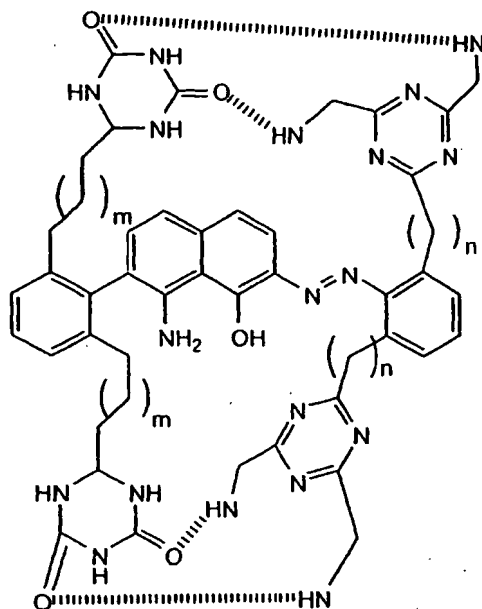
R4 is selected from the group consisting of H, SO₃H, COOH, CH₂SO₃H, CH₂COOH, C₂H₄SO₃H and C₂H₄COOH.

; and

printing said ink on a printing medium by means of an ink-jet pen.

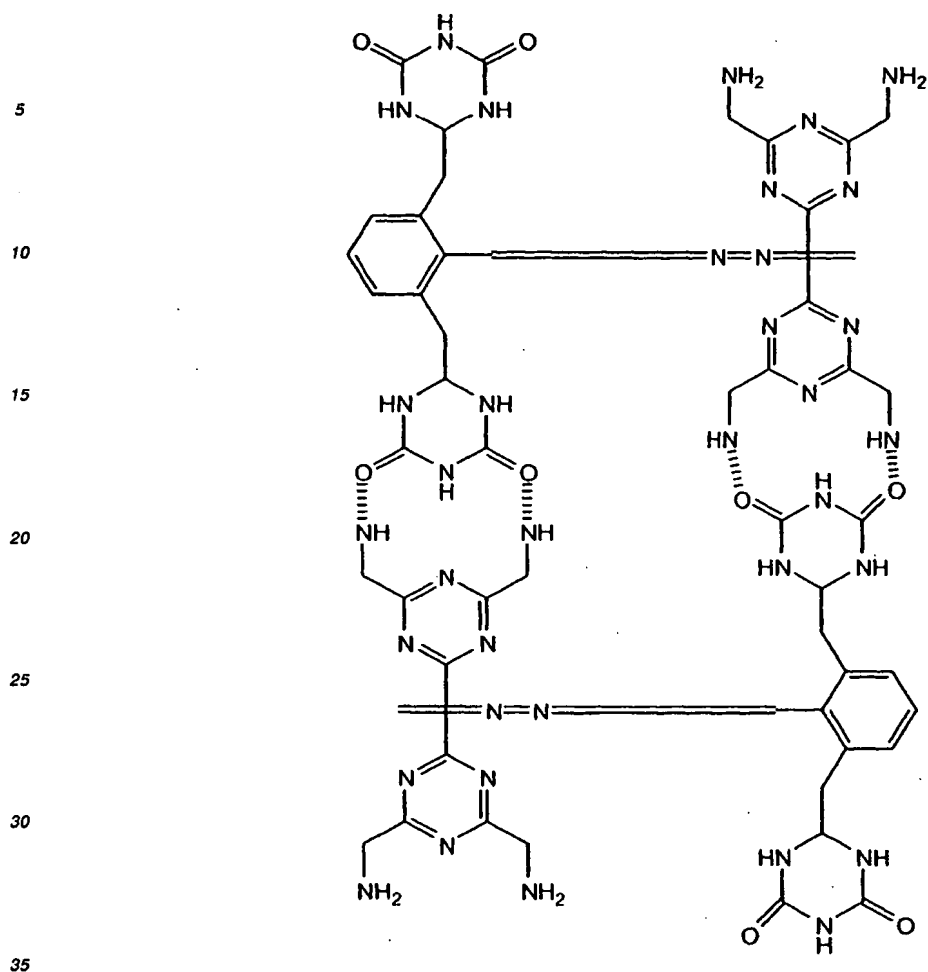
[0010] Furthermore, the present invention relates to a method for ink-jet printing, comprising:

providing at least one magenta ink containing at least one magenta dye having a visible light absorbance of 0.01 to 0.57 at λ_{\max} at a 1:10,000 dilution in water and having a structure as follows:



30 **[0011]** Additionally the present invention relates to a method for ink-jet printing, comprising:

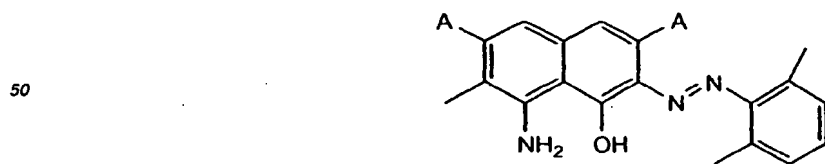
providing at least one magenta ink containing at least one magenta dye having a visible light absorbance of 0.01 to 0.57 at λ_{max} at a 1:10,000 dilution in water and having a structure as follows:



wherein

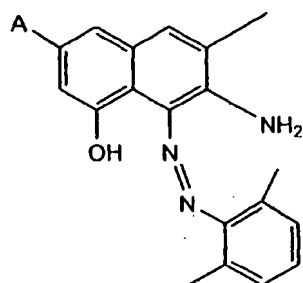


is an azo dye structure



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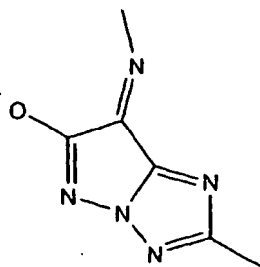
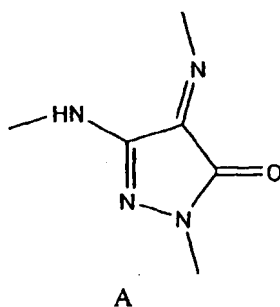
wherein A is selected from H and SO₃H,
or a gamma-acid based dye structure



wherein A is selected from H and SO₃H
; and

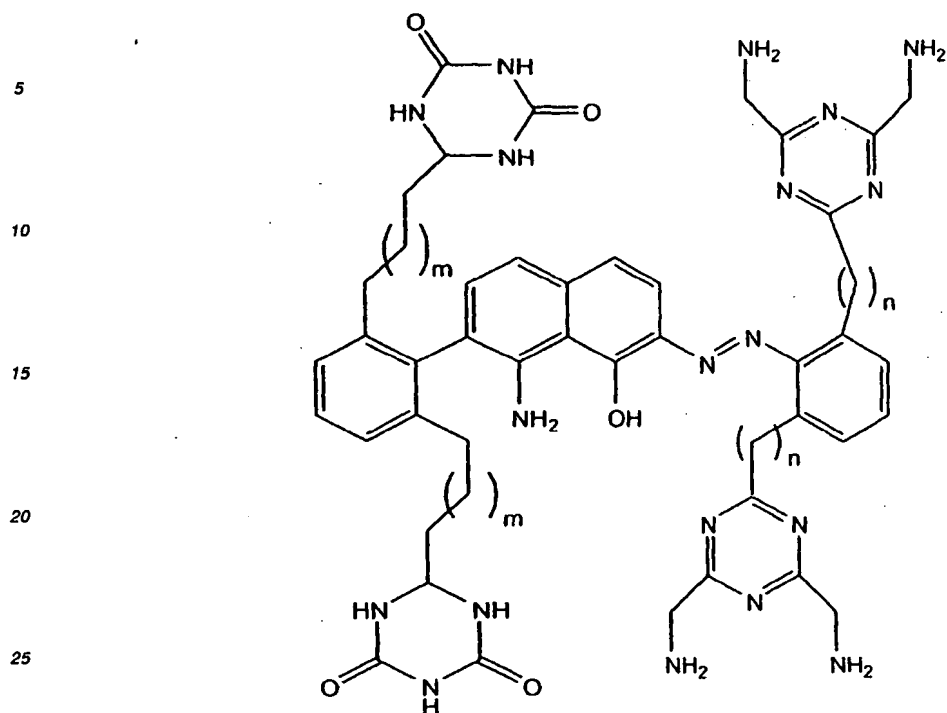
printing said ink on a printing medium by means of an ink-jet pen.

[0012] Also the present invention relates to a method of stabilizing chromophore dyes containing imino groups, the imino groups selected from the group consisting of imino groups A and B:

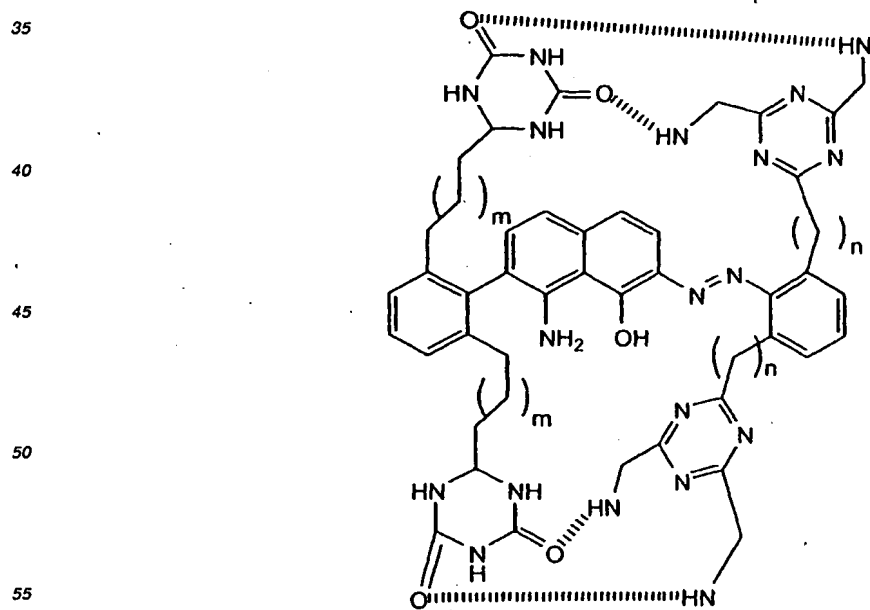


the method comprising adding steric groups to protect imino carbons, the steric groups being selected from phenyl, methyl, ethyl, isopropyl, fluoride, chloride, bromide and iodide.

[0013] Furthermore, the present invention relates to a method of stabilizing chromophore dyes comprising arms ending in at least one of cyanuric and melamine groups:

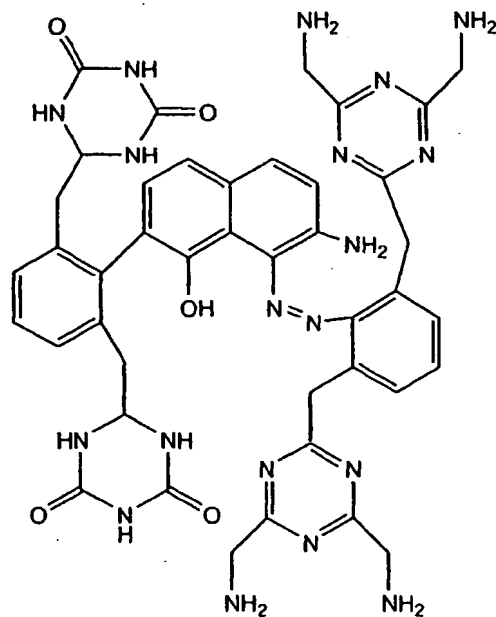
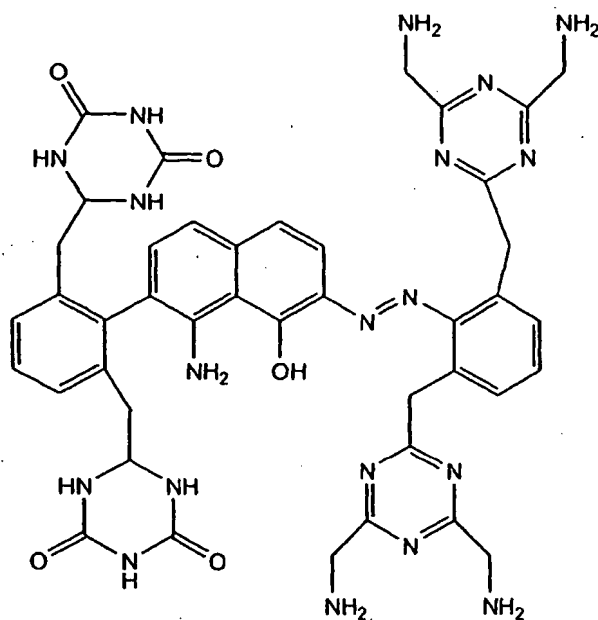


30 wherein m and n are from 0 to 4 added carbons.
the method comprising forming intramolecular hydrogen bonds between the cyanuric and melamine groups:

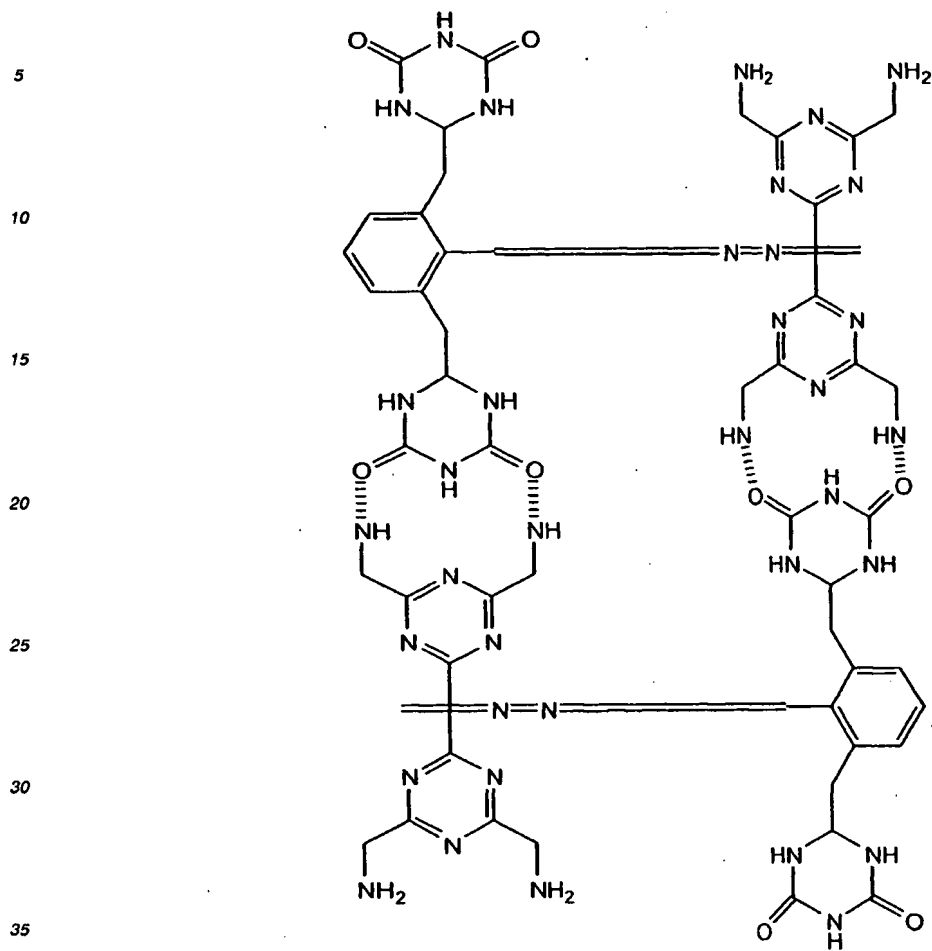


wherein m and n have from 0 to 4 added carbons.

[0014] Also, the present invention relates to a method of stabilizing chromophore dyes with one of the following structures comprising arms ending in at least one of cyanuric and melamine groups:



the method comprising forming intermolecular hydrogen bonds between the cyanuric and melamine groups of two different dye molecules:



wherein

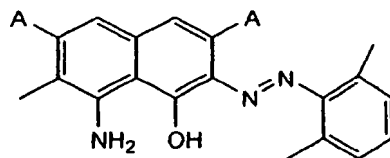
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is an azo dye structure

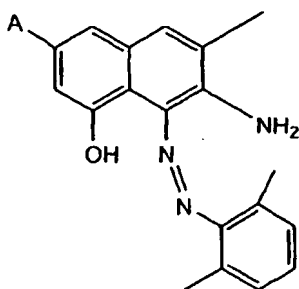
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wherein A is selected from H and SO₃H
or a gamma acid based dye structure

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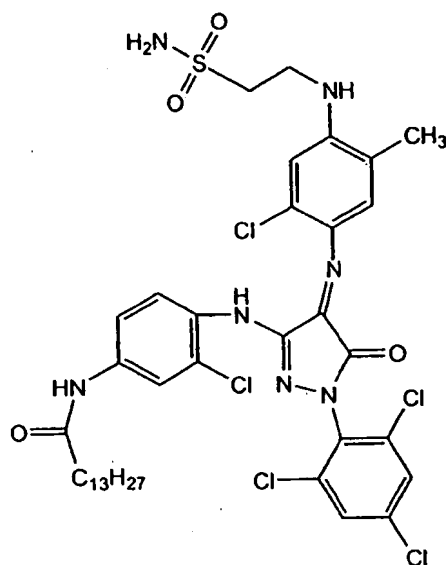


wherein A is selected from H and SO₃H.

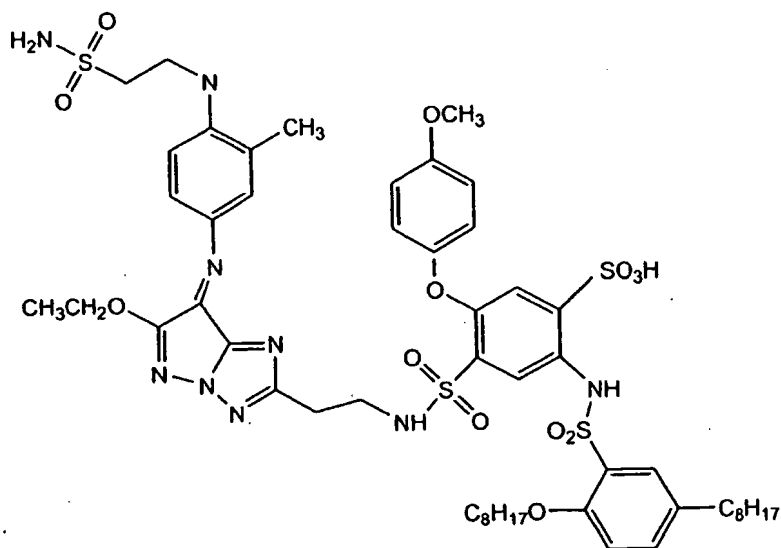
DETAILED DESCRIPTION OF THE INVENTION

[0015] The invention described herein is directed to dyes for use with commercially available ink-jet printers such as Design Jet® liner printers, manufactured by Hewlett-Packard Company, of Palo Alto, California. More specifically, a specific dye for formulating the magenta is disclosed. The dye enables the production of high-quality print and excellent lightfastness. The inks formulated according to the invention produce images having color appearance that meets commercial requirements for color accuracy and durability.

[0016] One of the most stable photographic systems on the market today is Fuji film and print media, which is reported to have a display life of 60 years. A search of patents by Fuji revealed that they have developed a novel class of dyes, which when used in photographic media, were very stable. Structures 1 and 2 are examples of such dyes:



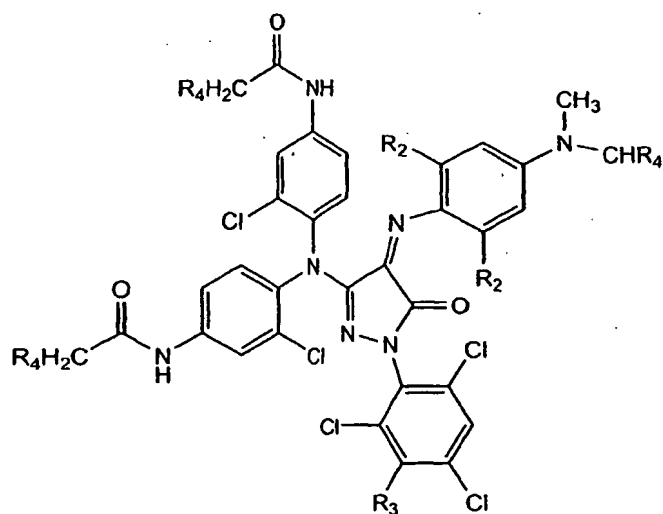
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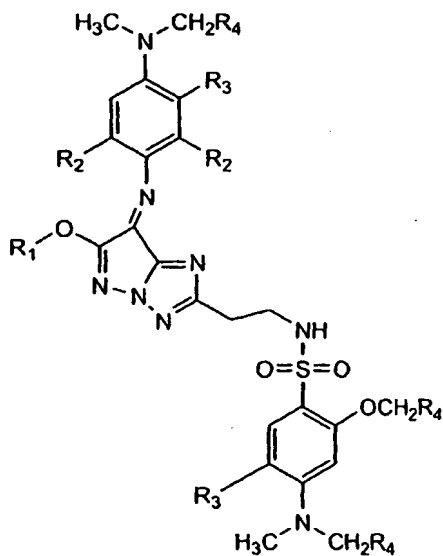
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[0017] Recognizing that the environment around the dye plays a very large role in dye stability, HP isolated the magenta dye from developed Fuji Crystal Archive photographic media and investigated its stability on a typical glossy ink jet medium. It was found not to be very stable toward light. Further, it is known that these azopyrazolone dyes can be attacked by ozone at the imine carbon. Thus, at first glance, this class of dye does not appear to be very interesting from an ink jet application standpoint. However, given that the chemistry of this class of dye is well known and it has a very good color, it is an excellent choice to pursue the concept of steric protection.

[0018] If all of the large "ballast" groups are stripped away that are present in typical photographic dyes to leave the basic chromophore and attach groups to provide steric protection of the imine carbon, the dyes shown in Structures 3 and 4 are produced



3



4

[0019] In structure 3, the phenyl group attached to the imino N at C-4 has ortho-methyl groups, which will inhibit formation of tetrahedral N during ozonolysis. Similarly, the C-5 nitrogen has two phenyl groups with ortho chlorines attached to make approach to C-5 more difficult. In an analogous manner, the azopyrasolotriazole dye (structure 2) has been modified to produce structure 4. In addition to the same ortho-methyl groups on the imino phenyl ring, oxygen at C-8 has an isopropyl instead of an ethyl group.

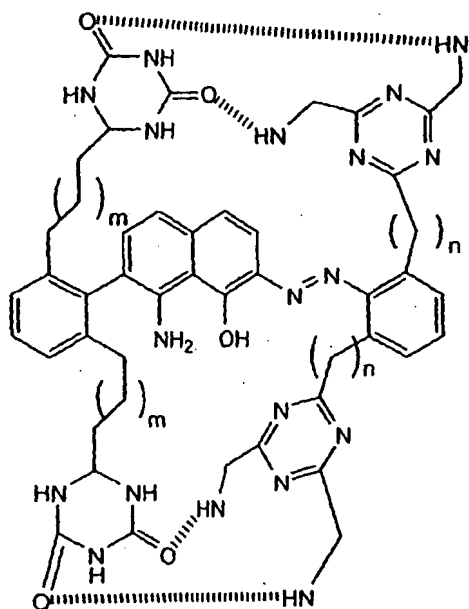
[0020] Molecular modeling (Hyperchem) of structure 3 shows that the approach to the imine carbon (or to the entire pyrazolone ring) is very hindered. Structure 1 shows the energy minimized structure.

[0021] A remaining challenge is to make these dyes water-soluble. Two options appear likely. One is to sulfonate one or more of the aromatic rings. Second is to change the acetamide groups to contain a water-solubilizing group, such as COOH, SO₃H, or polyether.

[0022] Further, it has been reported that spiroindane compounds when added to solutions of these dyes improve their lightfastness. It is speculated that the spiro materials act as singlet excited state quenchers. Thus, similar type additives could be added to these dyes either in the ink or in the media itself. Such work is the subject of a recent patent application by the same inventor, serial no. 09/662,950 filed on September 15, 2000.

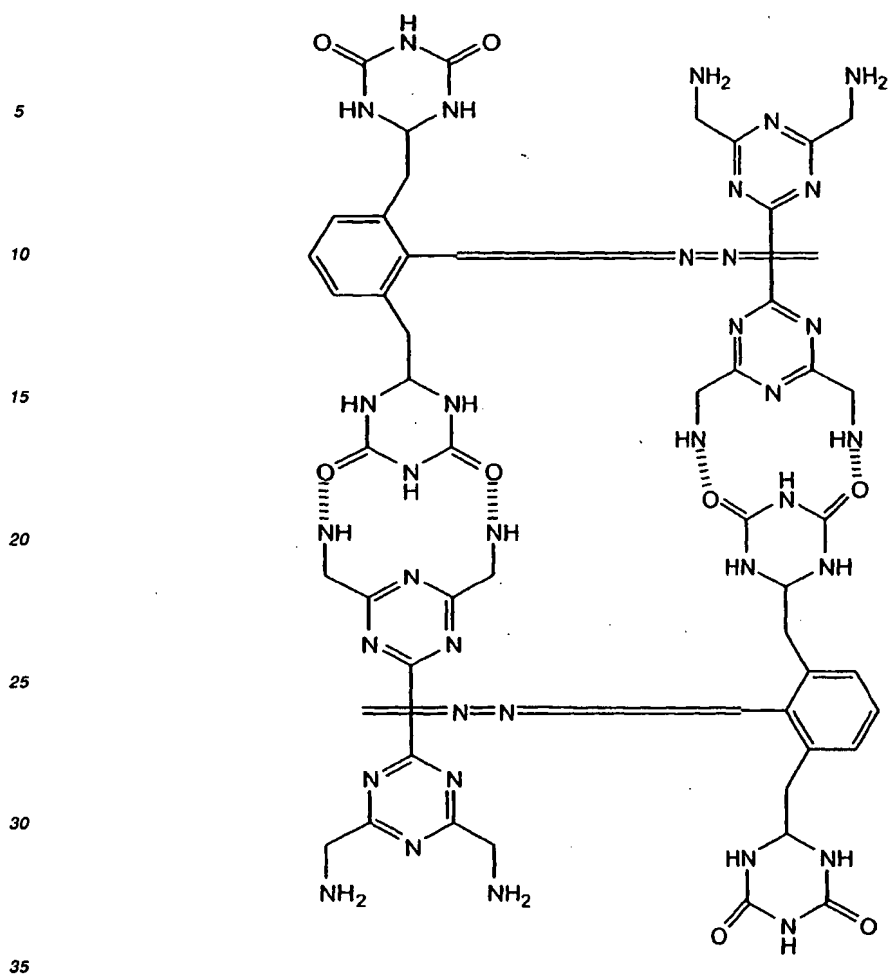
[0023] Another approach to providing steric protection of dyes is to encase them inside some structure. One method of doing this is to construct bridges that cross over above and below the imine or azo plane. However, synthetically, such structures are very challenging to make. An alternate method of doing this is to use the concept of "self-assembly". In this approach, the dye is constructed so that it contains arms that spontaneously form bridge like structures. This area of chemistry is extensive and recently reviewed. The driving force to make the bridge structure is the formation of several hydrogen bonds, although other methods such as metal chelation are also possible.

[0024] Using a proto-typical acid azo dye, complementary arms can be attached so that they form hydrogen bonds with each other. This process forms the protecting bridge. Such a structure is shown in structure 5, where the cyanuric and melamine groups can form H-bonds to each other above and below the plane of the naphthalene ring. This effectively "encapsulates" the dye. Space filling models (HGS) show that this arrangement is possible.



wherein m and n are from 0 to 4 added carbons.

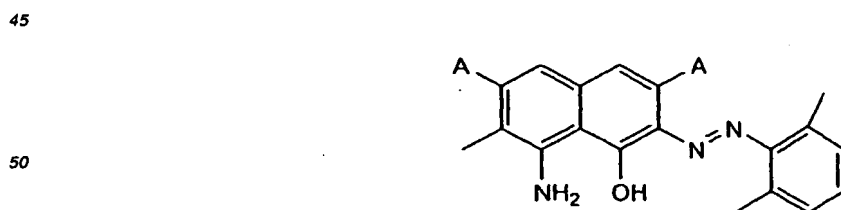
[0025] An alternate approach to this methodology is to shorten the alkyl chains that attach the cyanuric acid groups. This precludes intra-molecular H-bonding to the melamine group, but allows inter-molecular H-bonding. A head to tail stacking of the dye molecules then results. This enforced aggregation of the dye protects the dye for obvious steric reasons. Further, dye aggregation has been shown to improve light stability. This stacked structure is shown in Structure 6.



wherein

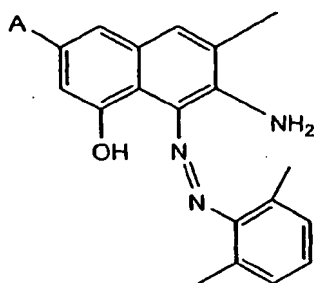


is an azo dye structure



55

wherein A is selected from H and SO₃H,
or a gamma acid based dye structure



wherein A is selected from H and SO_3H .

[0026] The present magenta aqueous ink compositions each comprise in general from about 0.1 to about 5 wt % of at least one dye, and a vehicle comprising the following components (in wt % of total ink composition): from about 5 to about 30 wt % of at least one organic solvent; 0 to about 2.0 wt % of at least one component independently selected from the group consisting of surfactants, buffers, biocides, and metal chelators; and the balance water. All concentrations herein are in weight percent of total ink composition unless otherwise indicated. The purity of all components is that employed in normal commercial practice for ink-jet inks.

Vehicle

[0027] The inks of the present invention comprise an aqueous vehicle comprising the following components (in wt % of total ink composition): from about 5 to about 30 wt % of at least one water soluble organic solvent; 0 to about 2.0 wt % of at least one component independently selected from the group consisting of surfactants, buffers, biocides, and metal chelators; and the balance water.

Organic Solvent

[0028] The inks of the present invention comprise from about 5 to about 30 wt % organic solvent. More preferably, the inks comprise from about 8 to about 20 wt % organic solvent, with a concentration from about 9 to about 15 wt % being the most preferred. The water soluble organic solvents suitably employed in the present ink-jet ink compositions include any of, or a mixture of two or more, of such compounds as nitrogen-containing heterocyclic ketones, such as 2-pyrrolidone, N-methyl-pyrrolid-2-one (NMP), 1,3-dimethylimidazolid-2-one, and octyl-pyrrolidone; diols such as ethanediols (e.g., 1,2-ethandiol), propanediols (e.g., 1,2-propanediol, 1,3-propanediol, 2-ethyl-2-hydroxy-methyl-1,3-propanediol, ethylhydroxy-propanediol (EHPD), butanediols (e.g., 1,2-butanediol, 1,3-butanediol, 1,4-butanediol), pentanediols (e.g., 1,2-pentanediol, 1,5-pentanediol), hexanediols (e.g., 1,6-hexanediol, 2,5-hexanediol, 1,2-hexanediol), heptanediols (e.g., 1,2-heptanediol, 1,7-heptanediol), octanediols (e.g., 1,2-octanediol, 1,8-octanediol); glycols and thioglycols, commonly employed in ink-jet inks, such as polyalkylene glycols such as polyethylene glycols (e.g., diethylene glycol (DEG), triethylene glycol, tetraethylene glycol), polypropylene glycols (e.g., dipropylene glycol, tripropylene glycol, tetrapropylene glycol), polymeric glycols (e.g., PEG 200, PEG 300, PEG 400, PPG 400), and thiodiglycol; and glycol ethers such as dipropylene glycol monobutyl ether, propylene glycol monobutyl ether, and ethylene glycol monobutyl ether, diethylene glycol monohexyl ether.

Surfactant

[0029] The inks of the present invention optionally comprise 0 to about 2.0 wt % surfactant. More preferably, the inks comprise from about 0.1 to about 1.8 wt % surfactant, with a concentration from about 0.8 to about 1.5 wt % being the most preferred.

In the practice of the invention, one or more surfactants may optionally be used. Nonionic surfactants, such as secondary alcohol ethoxylates (e.g., Tergitol series available from Union Carbide Co.), non-ionic fluoro surfactants (e.g., FC170C available from 3M, non-ionic fatty acid ethoxylate surfactants (e.g., Alkamul PSMO-20 available from Rhone-Poulenc), non-ionic silicone surfactants (e.g., SilwetL7600 available from Osi Specialties, Inc. Danbury, Conn.), and fatty amide ethoxylate surfactants (e.g., Aldamide L203 available from Rhone-Poulenc) are preferred, with secondary alcohol ethoxylates being the most preferred. In the practice of the invention, the surfactant serves to prevent color to color bleed by increasing the penetration of the inks into the print medium, and to improve the spread of the ink on polymer coated media. Secondary alcohol ethoxylates are nonionic surfactants and are commercially available, for

example, from Union Carbide Co. (Houston, Tex.) as the Tergitol series, such as Tergitol 15-S-5 and Tergitol 15-S-7.

[0030] The secondary alcohol ethoxylates contain (a) an aliphatic chain having a prescribed number of carbon atoms in the chain, and (b) a prescribed number of ethoxylated units. These ethoxylates are commercially available as mixtures of ethoxylates, and so are described in terms of the predominance of a given compound. Secondary alcohol ethoxylates suitably employed in the practice of the invention predominantly have from about 12 to about 18 carbon atoms in the aliphatic chain, while the number of ethoxylated units is predominantly in the range of from about 4 to about 8 units. Thus, "Tergitol 15-S-5" represents a secondary alcohol ethoxylate surfactant predominantly having about 15 carbons in its aliphatic chain and about 5 ethoxylated units. Tergitol 15-S-5 and Tergitol 15-S-7 are the preferred surfactants.

Buffer

[0031] The inks of the present invention optionally comprise 0 to about 1.5 wt % buffer. More preferably, the inks comprise from about 0.1 to about 0.5 wt % buffer, with a concentration from about 0.1 to about 0.3 wt % being the most preferred.

Buffers employed in the practice of the invention to modulate pH can be organic-based biological buffers or inorganic buffers, preferably, organic-based. Further, the buffers employed should maintain a pH ranging from about 3 to about 9 in the practice of the invention, preferably about 6.5 to about 8 and most preferably from about 7.5 to 8.5. Examples of preferably-employed buffers include Trizma Base, available from companies such as Aldrich Chemical (Milwaukee, Wis.), 4-morpholineethanesulfonic acid (MES), b-hydroxy-4-morpholinepropanesulfonic acid (MOPSO), and 4-morpholinepropanesulfonic acid (MOPS).

Metal Chelator

[0032] The inks of the present invention optionally comprise 0 to about 1.5 wt % metal chelator. More preferably, the inks comprise from about 0.1 to about 0.5 wt % metal chelator, with a concentration from about 0.1 to about 0.3 wt % being the most preferred.

[0033] Metal chelators employed in the practice of the invention are used to bind transition metal cations that may be present in the ink. Examples of preferably-employed metal chelators include: Ethylenediaminetetraacetic acid (EDTA), Diethylenetriaminepentaacetic acid (DTPA), trans-1,2-diaminocyclohexanetetraacetic acid (CDTA), (ethylenedioxy) diethylenedinitrilotetraacetic acid (EGTA), or other chelators that can bind transition metal cations. More preferably, EDTA, and DTPA; and most preferably EDTA in its disodium salt form is employed in the practice of the invention.

Biocide

[0034] The inks of the present invention optionally comprise 0 to about 1.5 wt % biocide. More preferably, the inks comprise from about 0.1 to about 0.5 wt % biocide, with a concentration from about 0.1 to about 0.3 wt % being the most preferred.

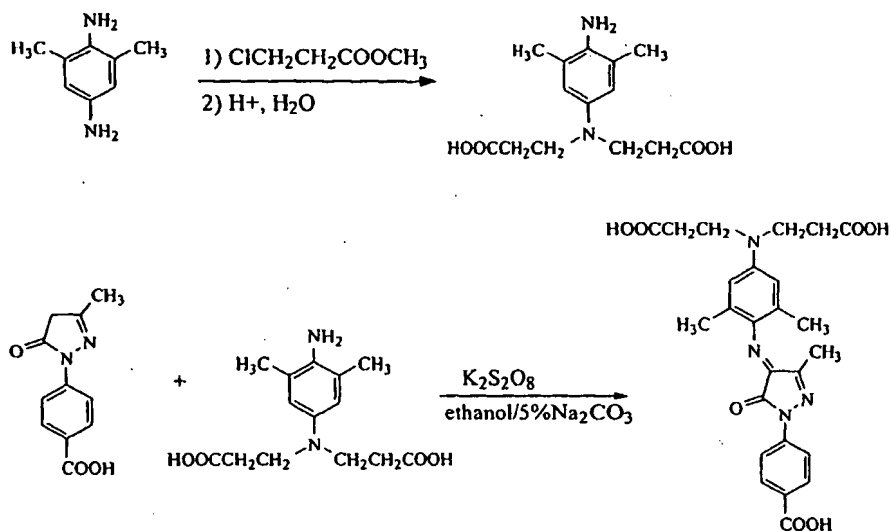
Any of the biocides commonly employed in ink-jet inks may be employed in the practice of the invention, such as Nuosept 95, available from Huls America (Piscataway, N.J.); Proxel GXL, available from Zeneca (Wilmington, Del.); and glutaraldehyde, available from Union Carbide Company (Bound Brook, N.J.) under the trade designation Ucarcide 250. Proxel GXL is the preferred biocide.

The specific ink set disclosed herein is expected to find commercial use in ink-jet color printing.

EXAMPLES

Example 1

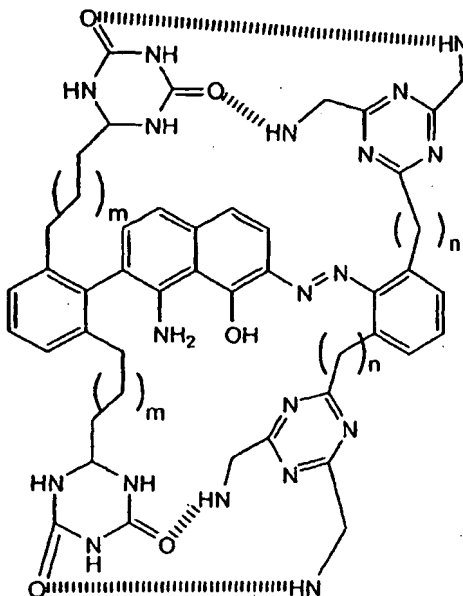
[0035] A pyrazolone azomethine dye of the present invention, is synthesized as shown below:



[0036] The desired hindered phenylenediamine is made by treating 2,5-dimethyl-1,4-phenylenediamine with methyl-3-chloropropanate and hydrolyzing the resulting ester to the acid. In the above formula, the pyrazolone azomethine dye [4-(3-methyl-4-)4-(N,N-di-(ethylsulfonic acid) amino)-1-phenylimino)-5-oxo-2-pyrazotin-yl)-benzoic acid] was prepared by adding 0.6 grams of potassium persulfate to a stirred mixture of 4-(3-methyl-5-oxo-2-pyrazolin-1-yl)-benzoic acid (1 mmol), N,N-diethylsulfonic acid)-1,4-phenylenediamine (0.25 g), methanol (10 mL), and sodium carbonate in water (5%; 20 mL). The mixture was stirred for about 40 minutes and then additional water (70 mL) was added. The pyrazolone azomethine dye was collected by filtration, dried and recrystallized with methanol or ethanol.

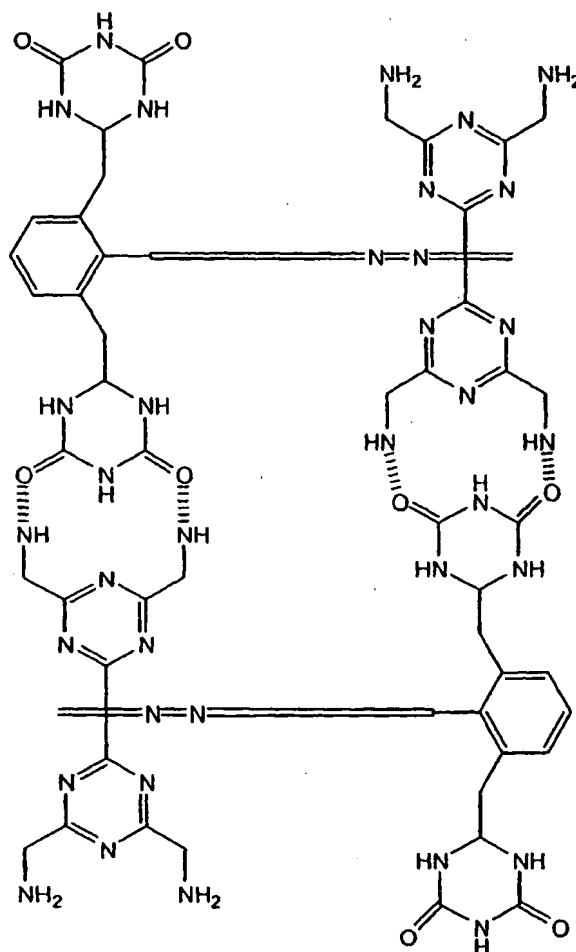
Claims

1. A magenta ink for ink-jet printing, comprising a dye having the following structure:



wherein m and n are from 0 to 4 added carbons.

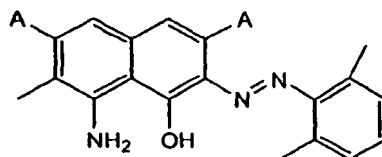
2. A magenta ink for inkjet printing comprising a dye having the following structure:



wherein



is an azo dye structure

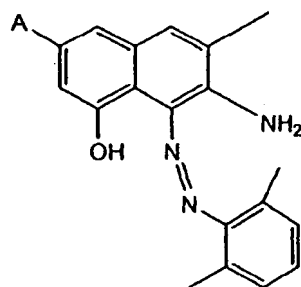


wherein A is selected from H and SO_3H ,

or a gamma acid based dye structure

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wherein A is selected from H and SO₃H.

3. A method of stabilizing chromophore dyes comprising arms ending in at least one of cyanuric and melamine groups:

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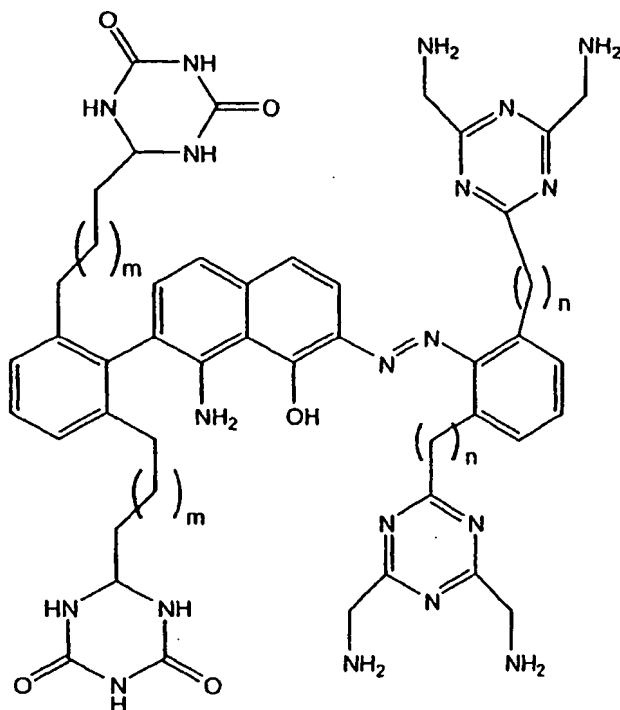
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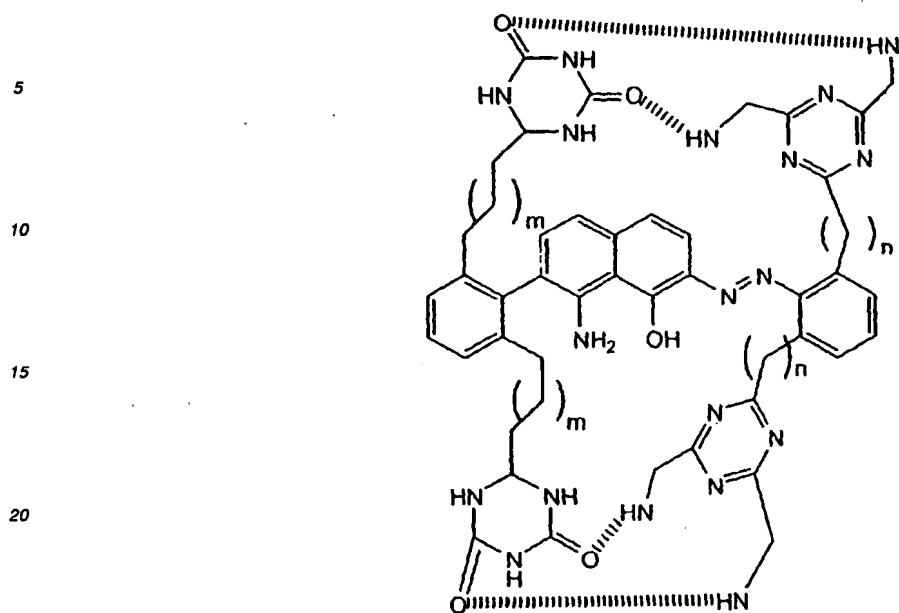


wherein m and n are from 0 to 4 added carbons.

the method comprising forming intramolecular hydrogen bonds between the cyanuric and melamine groups

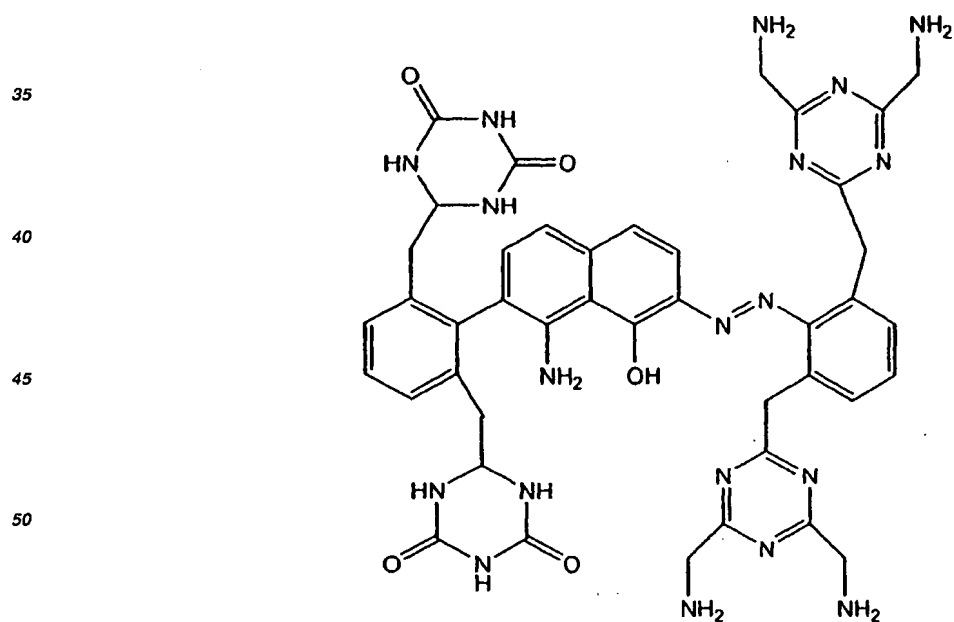
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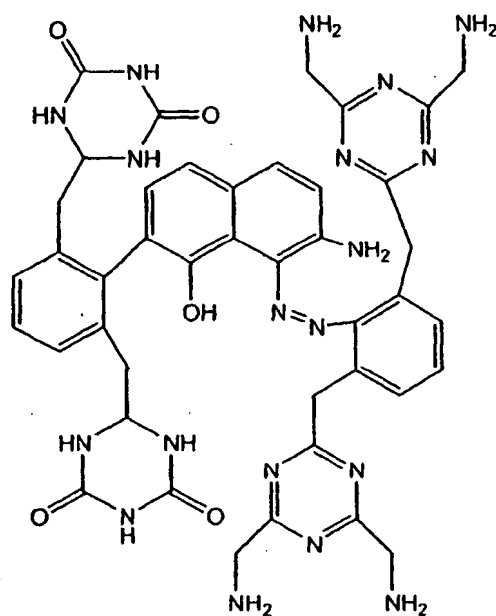
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wherein m and n are from 0 to 4 added carbons.

4. A method of stabilizing chromophore dyes with one of the following structures comprising arms ending in at least one of cyanuric and melamine groups:





the method comprising forming intermolecular hydrogen bonds between the cyanuric and melamine groups of two different dye molecules:

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wherein

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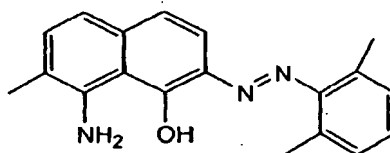
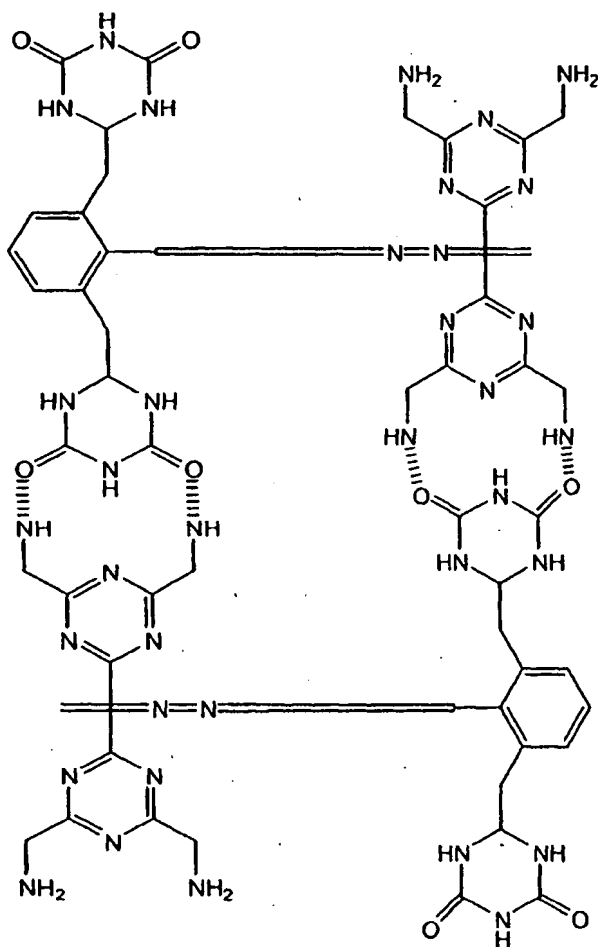
is an azo dye structure

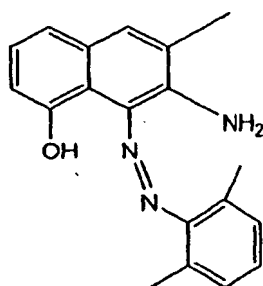
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or a gamma acid based dye structure

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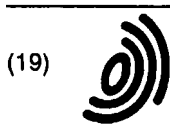
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(54) **Dye-based ink jet ink compositions having improved stability and light fastness**

(57) An aqueous ink jet ink is disclosed which comprises an effective amount of an azomethine dye having at least one water solubilizing functional group covalently attached thereto. The water solubilizing functional group can either be directly attached to the azomethine dye and/or can be attached to the azomethine dye through an electrophilic coupling moiety. If an organic spacer group is used to separate the water solubilizing functional group from azomethine dye or the electrophilic coupling moiety, then straight and branched

chained alkyl groups having from about 1 to 10 carbon atoms is preferred. Preferred azomethine dyes can be pyrazolone azomethines, pyrazolotriazole azomethines, and combinations thereof. Additionally, an aqueous ink jet ink is disclosed comprising an effective amount of a dye-based colorant and an essentially water soluble spiroindane additive for improving light fastness and stability of the dye-based colorant.

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Description**FIELD OF THE INVENTION**

5 **[0001]** The present invention is drawn to dye-based ink jet ink compositions having improved stability and light fastness.

BACKGROUND OF THE INVENTION

10 **[0002]** In recent years, computer printer technology has evolved to a point where very high resolution images can be transferred to various types of media, including paper. One particular type of printing involves the placement of small drops of a fluid ink onto a media surface in response to a digital signal. Typically, the fluid ink is placed or jetted onto the surface without physical contact between the printing device and the surface. Within this general technique, the specific method that the ink jet ink is deposited onto the printing surface varies from system to system, and can include continuous ink deposit and drop-on-demand ink deposit.

15 **[0003]** With regard to continuous printing systems, inks used are typically based on solvents such as methyl ethyl ketone and ethanol. Essentially, continuous printing systems function as a stream of ink droplets ejected and directed by a printer nozzle. The ink droplets are directed additionally with the assistance of an electrostatic charging device in close proximity to the nozzle. If the ink is not used on the desired printing surface, the ink is recycled for later use. With regard to drop-on-demand printing systems, the ink jet inks are typically based upon water and glycols. Essentially, with these systems, ink droplets are propelled from a nozzle by heat or by a pressure wave such that all of the ink droplets ejected are used to form the printed image.

20 **[0004]** There are several reasons that ink jet printing has become a popular way of recording images on various media surfaces, particularly paper. Some of these reasons include low printer noise, capability of high speed recording, and multi-color recording. Additionally, these advantages can be obtained at a relatively low price to consumers. However, though there has been great improvement in ink jet printing, accompanying this improvement are increased demands by consumers in this area, e.g., higher speeds, higher resolution, full color image formation, increased stability, etc. As new ink jet inks are developed, there have been several traditional characteristics to consider when evaluating the ink in conjunction with a printing surface or substrate. Such characteristics include edge acuity and optical density of the image on the surface, dry time of the ink on the substrate, adhesion to the substrate, lack of deviation of ink droplets, presence of all dots, resistance of the ink after drying to water and other solvents, long term storage stability, and long term reliability without corrosion or nozzle clogging. Though the above list of characteristics provides a worthy goal to achieve, there are difficulties associated with satisfying all of the above characteristics. Often, the inclusion of an ink component meant to satisfy one of the above characteristics can prevent another characteristic from being met. Thus, most commercial inks for use in ink jet printers represent a compromise in an attempt to achieve at least an adequate response in meeting all of the above listed requirements.

30 **[0005]** In general, ink jet inks are either dye- or pigment-based inks. Dye-based ink jet inks generally use a liquid colorant that is usually water-based to turn the media a specific color. Because of their makeup, dye-based inks are usually not waterproof and tend to be more affected by UV light. This results in the color changing over time, or fading. For optimum performance, this type of ink has often required that the proper media be selected in accordance with the application, thus, reducing the choice of media for printing. Conversely, pigmented inks typically use a solid colorant to achieve color. In many cases, the line quality and accuracy of plots produced by pigment-based inks are usually superior to that of dye-based inks. With pigmented inks, solid particles adhere to the surface of the substrate. Once the water in the solution has evaporated, the particles will generally not go back into solution, and are therefore more waterproof. In addition, pigmented inks are much more UV resistant than dye-based inks, meaning that it takes much longer for noticeable fading to occur. Though pigmented inks, in some areas, exhibit superior characteristics, dyes tend to run cleaner, provide better yield, offer better particle size, and are easier to filter. Thus, dye-based inks have been more often used for common applications and have tended to be more chromatic and provide more highly saturated colors.

45 **[0006]** In order for ink jet prints to effectively compete with silver halide photography, one important improvement that must occur is that ink jet inks must improve their ability to remain stable to light exposure for longer periods of time. At this point in time, photographs typically will last much longer under prolonged light exposure, i.e., about 14-18 years under fluorescent light exposure. Conversely, some of the best ink jet printers will produce prints that last for only about 6-8 years under similar conditions. Particularly, with respect to dye-based ink jet ink, the phenomenon of discoloration occurs even more readily than is typical for pigment-based ink jet inks. However, as described above, dye-based inks are sometimes preferred because they are very convenient to use and have good distinction of color.

50 **[0007]** In the photographic industry, technologies have been developed which have been reported to last much longer than the typical 14-18 years, and even up to 60 years. Such long lasting ink stability has been attributed to a very stable

magenta dye which is, in part, the subject of U.S. Patent 5,242,785. That patent reports many new dyes and additives that have very good light fastness (2% dye loss after 16.5 years of simulated light exposure). However, though these dyes are very stable under prolonged light exposure, these dyes are not water-soluble and contain long chain organic groups necessary for anchoring dyes in photographic media. Such structures are not useable in aqueous-based ink jet systems.

[0008] Thus, it would be useful to provide aqueous ink jet inks for printing on media such that the inks are more stable under prolonged light exposure and/or exhibit good light fastness. This can be accomplished by providing dyes and/or additives for aqueous ink jet inks that improve these and other important properties.

SUMMARY OF THE INVENTION

[0009] An aqueous ink jet ink is disclosed which comprises an effective amount of an azomethine dye having at least one water solubilizing functional group covalently attached thereto wherein the water solubilizing functional group is directly attached to the azomethine dye or is attached to the azomethine dye through an electrophilic coupling moiety. If an organic spacer group is used to separate the water solubilizing functional group from azomethine dye or the electrophilic coupling moiety, then straight and branched chained alkyl linkers or spacers having from about 1 to 10 carbon atoms are preferred. Preferred azomethine dyes can be pyrazolone azomethines, pyrazolotriazole azomethines, and combinations thereof. Additionally, an aqueous ink jet ink is disclosed comprising an effective amount of a dye-based colorant and an essentially water soluble spiroindane additive for improving light fastness and stability of various dye-based colorants.

DETAILED DESCRIPTION OF THE INVENTION

[0010] Before the present invention is disclosed and described, it is to be understood that this invention is not limited to the particular process steps and materials disclosed herein because such process steps and materials may vary somewhat. It is also to be understood that the terminology used herein is used for the purpose of describing particular embodiments only. The terms are not intended to be limiting because the scope of the present invention is intended to be limited only by the appended claims and equivalents thereof.

[0011] It must be noted that, as used in this specification and the appended claims, the singular forms "a", "an", and "the" include plural referents unless the content clearly dictates otherwise.

[0012] The term "water solubilizing functional group" is meant to define a group imparting hydrophilic properties such as sulfonic acids, carboxylic acids, sugars, amines, polyethers, phosphates, boronic acids, and combinations thereof, or other similar hydrophilic groups.

[0013] The term "electrophilic coupling moiety" refers to a linkage through which the water solubilizing functional group can be coupled to an aromatic ring of an azomethine dye or to a linking spacer group that is, in turn, coupled to an aromatic ring of an azomethine dye. Representative of suitable coupling moieties are members selected from the group consisting of amide, amine, sulfonamide, sulfonyl, and ester linkages.

[0014] The term "spacer" is meant to include an aliphatic straight or branched chain hydrocarbon having from about one to ten carbon atoms that link the water solubilizing functional group to the azomethine dye. The spacer can be linked to either the water solubilizing functional group or to an aromatic ring of the azomethine dye through an electrophilic coupling moiety.

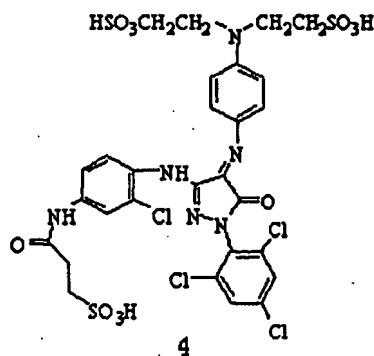
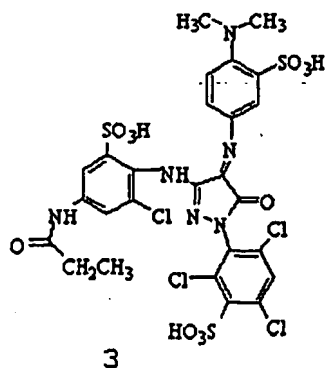
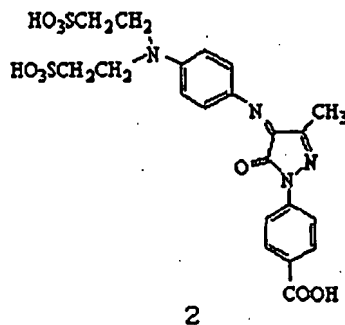
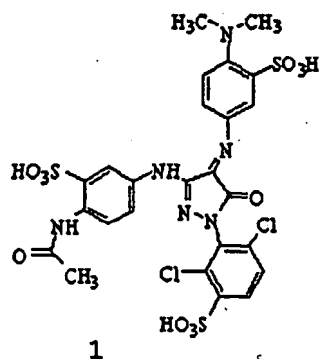
[0015] With regard to any structure where a water solubilizing functional group has been added, the term "soluble" includes any structure that has been solubilized to the extent that it is functional in an aqueous based ink.

[0016] With this in mind, an aqueous ink jet ink comprising an effective amount of an azomethine dye having at least one water solubilizing functional group covalently attached thereto is disclosed. The water solubilizing functional group can be either directly attached to the azomethine dye and/or can be attached through an electrophilic coupling moiety. If an organic spacer is used to separate the water solubilizing functional group from azomethine dye or the electrophilic coupling moiety, then straight and branched chained alkyl spacers having from about 1 to 10 carbon atoms are preferred. The azomethine dye is preferably present in the ink jet ink at from about 0.1% to 10% by weight, though any effective amount may be used. Additionally, the azomethine dye is preferably selected from the group consisting of pyrazolone azomethines, pyrazolotriazole azomethines, and combinations thereof.

[0017] Since ink jet inks are typically water-based, at least one water solubilizing functional group must be attached to the azomethine dye in order to improve the solubility of the dyes. Preferably, a plurality of water solubilizing functional groups are covalently attached to the dyes. The water solubilizing functional group can be selected from the group consisting of sulfonic acids, carboxylic acids, sugars, amines, polyethers, phosphonic acids, boronic acids, and combinations thereof, though other groups functional for solubilizing the dyes can be used in conjunction with the present invention. In a preferred embodiment, sulfonic acid groups are covalently attached to the azomethine dyes either directly to an aromatic ring, or through an electrophilic coupling moiety.

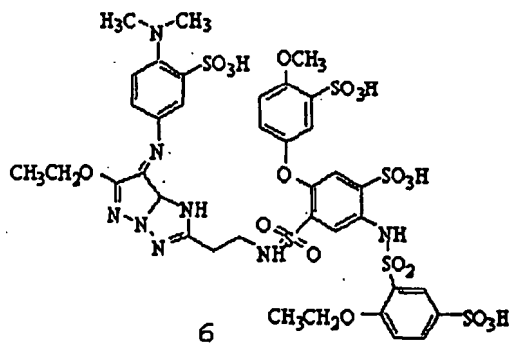
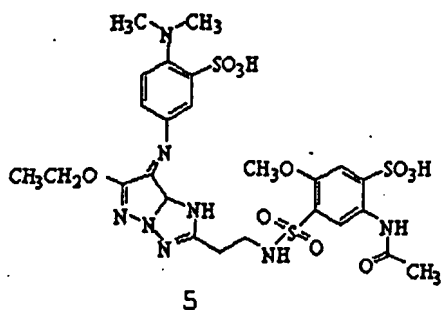
[0018] The water solubilizing functional group can be covalently attached to the azomethine dye in one or both of two preferred ways. First, the water solubilizing functional group can be covalently bonded directly to an aromatic ring on the dye. Alternatively, the water solubilizing functional group can be attached to the azomethine dye through an electrophilic coupling moiety such as an amide, an amine, a sulfonamide, a sulfonyl, or an ester. If two or more water solubilizing functional groups are attached to the azomethine dyes, in one embodiment, at least one water solubilizing functional group can be attached directly to an aromatic ring of the dye and at least one additional water solubilizing functional group can be covalently attached through an electrophilic coupling moiety.

[0019] Dyes 1 to 4 shown below provide examples of pyrazolone azomethine dyes that can be prepared in accordance with the present invention.



and

[0020] Additionally, dyes 5 and 6 shown below provide examples of pyrazolotriazole azomethine dyes that may be prepared in accordance with the present invention.



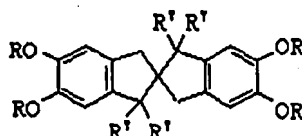
and

[0021] The pyrazolone azomethine and pyrazolotriazole azomethine structures shown above are not the only structures that are functional. These structures are merely meant to provide representative examples of functional structures. For example, though the pyrazolotriazole structures shown, i.e., dyes 5 and 6, are both pyrazolo-[1,2,4]-triazole structures, pyrazolo-[1,3,4]-triazole dye structures are also known and could be derivatized to likewise include water solubilizing functional groups in accordance with the present invention. Additionally, different water solubilizing functional groups can be used or different placement of water solubilizing functional groups can be effectuated, as long as the water solubilizing functional groups are not substantially substituted for groups that provide the color, light fastness, or other important dye function of the structure. For example, with regard to the dyes shown above, the groups that are believed to be essential to color stability and light fastness have been retained. Other groups have been replaced with sulfonic acid to improve the solubility of the structures. Additionally, in some dyes, certain appendages remain intact that can also be important in the dyes' light fastness properties. Note that the sulfonic acid groups (or other water solubilizing functional groups) do not necessarily need to be positioned on the aromatic rings. These groups can also be attached as part of various side chains through electrophilic coupling moieties, such as through an amide, amino, sulfonamide, sulfonyl, or ether linkages.

[0022] In addition to the azomethine dyes disclosed herein, lightfastness and stability can be enhanced in many different types of dye-based inks (including, but not limited to, the azomethine dyes disclosed herein) by the addition of certain additives. These various additives are stabilizing agents that are based upon a unique type of spiroindane compound which acts as an excited singlet state quencher for many dyes. When a dye is in an excited state, i.e., electrons at a higher energy level, degradation of the dye can occur. Thus, by using the spiroindane additives disclosed herein, the excited state of various dyes can be deactivated before they have substantial opportunity to degrade. Such action is believed to extend the stability and light fastness of the dyes with which the additive is mixed. Prior to the present disclosure, such spiroindane compounds were essentially water insoluble, and thus, have not been useful for use in aqueous ink jet inks. For example, tetra-hydroxy spiroindanes, which are not sufficiently soluble in water to be effectively used in ink jet inks, are currently available commercially.

[0023] It would be useful to prepare spiroindane additives for aqueous ink jet inks having similar properties as the tetrahydroxy spiroindanes currently known. Such additives can be prepared by modifying a tetra-hydroxy spiroindane by directly functionalizing the aromatic ring with appropriate water solubilizing functional groups, or preferably, by functionalizing the aromatic rings with water solubilizing functional groups through straight or branched spacers having from about 1 to 10 carbon atoms. More preferably, from 3 to 10 carbon atoms can be used in order to substantially maintain the quencher properties of the compound. One effective spacer is a straight chained propyl group.

[0024] Specifically, a spiroindane additive of the present invention can be defined as Formula 7 below:



Formula 7

wherein each R group can independently be H or contain a water solubilizing functional group, with the proviso that at least one R group contain a water solubilizing functional group. The water solubilizing functional group can be covalently attached to the aromatic ring or can be attached through a spacer. However, though only one is required, it is preferred that from 2 to 4 R groups contain a water solubilizing functional group. Additionally, R' can be independently selected from the group consisting of H and straight or branched chain alkyl having from about 1 to 5 carbon atoms.

[0025] If the water solubilizing functional group is attached through a spacer, then straight or branched carbon chains having from about 1 to 10 carbons atoms are functional, though from 3 to 10 carbon atoms are preferred. Specifically, it is preferred that when the R group is a spacer/water solubilizing functional group combination, then the R group of Formula 7 be independently selected from the group consisting of $-R^2SO_3H$, $-R^2COOH$, $-R^2N(CH_3)_3^+$, and $R^2(CH_2CH_2O)_nCH_2CH_2OR^3$, where R^2 can be 1 or 2 carbon atoms, but is preferably a straight or branched carbon chain having from 3 to 10 carbons. However, as mentioned, a straight three carbon chain (propyl) is the most preferred, particularly with respect to the use of sulfonic acid as the solubilizing group. In the case of the polyethylene oxide structure shown, n can be from 1 to 10 and R^3 can be H, CH_3 , or CH_2CH_3 . The water solubilizing functional groups can also be any other water solubilizing functional group that provides improved solubility. For example, groups including sugars, polyols, and pyridiniums, e.g., N-methylpyridinium, can be functional.

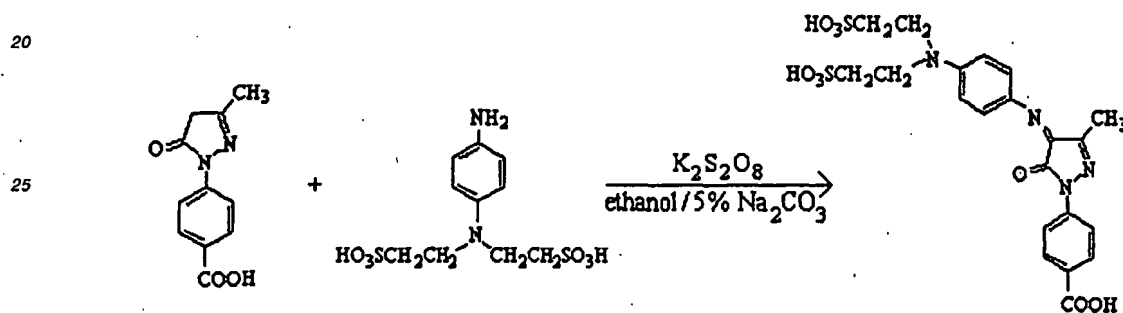
[0026] These spiroindane compounds, when incorporated into an aqueous dye-based ink, can be comprised of an effective amount of a dye-based colorant and an effective amount of the essentially water soluble spiroindane additive. However, about 1 to 10% by weight of the spiroindane additive is considered to be preferred. Additionally, though the stability and light fastness can be improved in many types of dye-based inks, stability and light fastness of the azomethine dyes of the present invention can further be improved by the spiroindane additives disclosed herein.

EXAMPLES

[0027] The following examples illustrate various formulations for preparing the ink jet ink compositions of the present invention, as well as provide data showing the effectiveness of adding the spiroindane additives disclosed herein. The following examples should not be considered as limitations of the present invention, but should merely teach how to make the best known ink jet ink formulations based upon current experimental data.

Example 1

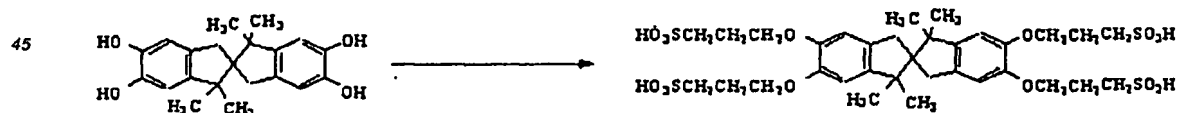
[0028] A pyrazolone azomethine dye of the present invention was synthesized as shown below:



[0029] In the above formula, the pyrazolone azomethine dye [4-(3-methyl-4-(4-(N,N-di(ethylsulfonic acid)amino)-1-phenylimino)-5-oxo-2-pyrazolin-1-yl)-benzoic acid] was prepared by adding 0.6 grams of potassium persulfate to a stirred mixture of 4-(3-methyl-5-oxo-2-pyrazolin-1-yl)-benzoic acid (1 mmol), N,N-di(ethylsulfonic acid)-1,4-phenylenediamine (0.25 g), methanol (10 mL), and sodium carbonate in water (5%; 20 mL). The mixture was stirred for about 40 minutes and then additional water (70 mL) was added. The pyrazolone azomethine dye was collected by filtration, dried, and recrystallized with methanol or ethanol.

Example 2

[0030] A spiroindane additive of the present invention was synthesized as described and shown below:



[0031] To a stirring suspension of NaH [5.88 g (60% dispersion in mineral oil), 4 eq.] in dimethyl sulfoxide (500 mL) was added 3,3',3'',3'''-tetramethyl-1,1'-spirobisindane-5,5',6,6'-tetraol [10.40 g (96%), 29.4 mmol] in small portions under argon via a solid addition funnel. After the addition was complete, the mixture was allowed to stir at room temperature for 20 hours and sodium 3-bromopropanesulfonate [40 g (97%), 6 eq.] was added in small portions. The reaction mixture was then warmed to 50°C and stirred until the reaction was complete (about 16 hours). Next, the reaction mixture was allowed to cool to room temperature and was added to 4.5 L of ethyl acetate with vigorous stirring. The suspension was filtered and the filter cake was air-dried. The collected solid was dissolved in benzene (400 mL) and 15% aqueous hydrochloric acid (200 mL) was added forming a biphasic mixture. This mixture was heated to reflux and water was removed by distillation. The benzene supernatant was then decanted from the deposited solids which

were dissolved in hot dimethyl sulfoxide (350 mL, 55°C) and filtered into ethyl acetate (3.5 L). The filtrate formed a precipitate which was filtered off and the collected solid was washed with ethyl acetate (100 mL). The collected solid was then triturated with ethanol (1 L), filtered, and washed with diethyl ether (500 mL). The filter cake was dried *in vacuo* to yield 22.80 g (94%) of product.

Example 3

[0032] Two samples of a magenta dye formulation known as AR81 [Acid Red 81 from the Color Index Name, available from Bayer; 3-(N-methylamino)-6-(4-sulfonic acid-1-amiobenzene)-2H,7H-benz[de]anthracen-2,7-dione, sodium salt] were tested for dye loss after being applied to paper. One of the two samples had 5% by weight of a water soluble spiroindane additive present and the other sample had no additive present. Each sample was imprinted onto two types of print media, i.e., HP Premium Plus Glossy and Mitsubishi 170. The four total ink sample/print media combinations were exposed to 60 Klux of cool-white fluorescent light for the equivalent of 6 years of normal exposure (450 lux per 12 day assumed as normal indoor light exposure). A dye loading of 3% (w/w) and an additive loading of 5% (w/w) was used. The ink vehicle consisted of (by weight) 8% 1,5-pentanediol, 6.5% 2-pyrrolidinone, 7.5% Trimethylolpropane, 1.5% TERGITOL™ 15-S-7, 0.5% TERGITOL™ 15-S-5, 0.2% FC-00, and 0.4% DOWFAX™ 8390. Each sample continued to be exposed to the fluorescent light until 20% dye loss had occurred in color patches having an initial optical density of 0.5. Table 1 below illustrates the results.

TABLE 1

PAPER	DYE ONLY Years for 20% dye loss	DYE + ADDITIVE years for 20% dye loss
HP Premium Plus Glossy	2.1	2.5
Mitsubishi 170	3.5	4.5

[0033] The data in Table 1 shows that the spiroindane additive has a positive effect on a magenta dye on two specific papers. The fact that this type of additive has a positive effect on the ink tested is significant because, in general, many additives do not work to improve properties of ink jet inks. This is likely due to the fact that additives and dyes do not remain in close proximity once printed on the media. Thus, these spiroindane additives are not only useful in ink jet ink formulations, but good results can also be achieved if these additives are incorporated directly into the ink receiving layer of certain print media.

[0034] While the invention has been described with reference to certain preferred embodiments, those skilled in the art will appreciate that various modifications, changes, omissions, and substitutions can be made without departing from the spirit of the invention. It is intended, therefore, that the invention be limited only by the scope of the following claims.

Claims

1. An aqueous ink jet ink comprising an effective amount of an azomethine dye having at least one water solubilizing functional group covalently attached thereto, and wherein said water solubilizing functional group is directly covalently attached to the azomethine dye or is covalently attached through an electrophilic coupling moiety.
2. The aqueous ink jet ink of claim 1 wherein the azomethine dye is present at from about 0.1 to 10% by weight and is selected from the group consisting of pyrazolone azomethine dyes, pyrazolotriazole azomethine dyes, and combinations thereof.
3. The aqueous ink jet ink of claims 1 or 2 wherein the water solubilizing functional group is selected from the group consisting of sulfonic acids, carboxylic acids, sugars, quaternary amines, polyethers, phosphoric acids, boronic acids, and combinations thereof.
4. The aqueous ink jet ink of claims 1 or 2 wherein the water solubilizing functional group is directly attached to the azomethine dye.
5. The aqueous ink jet ink of claims 1 or 2 wherein the water solubilizing functional group is covalently attached to the azomethine dye through an electrophilic coupling moiety selected from the group consisting of amides, amines, sulfonamides, sulfonyls, and esters.

6. The aqueous ink jet ink of claims 1 or 2 wherein the water solubilizing functional group is covalently attached to an aromatic ring or an electrophilic coupling moiety by a straight or branched carbon chain having from about 1 to 10 carbon atoms.

7. An aqueous ink jet ink comprising:

- a) an effective amount of a dye-based colorant; and
- b) from about 1 to 20% by weight an essentially water soluble spiroindane additive for improving light fastness and stability of the dye-based colorant.

8. The aqueous ink jet ink of claim 7 wherein the spiroindane additive is defined by the structure:



wherein R is independently selected from the group consisting of H and a constituent containing a water solubilizing functional group, with the proviso that at least one R group contain a water solubilizing functional group, and wherein R' is independently selected from the group consisting of H and straight or branched chain alkyl groups having from about 1 to 5 carbon atoms.

9. The aqueous ink jet ink of claims 8 wherein from 2 to 4 R groups be independently selected from the group consisting of $-R^2SO_3H$, $-R^2COOH$, $-R^2N(CH_3)_3^+$, $R^2(CH_2CH_2O)_nCH_2CH_2OR^3$, where R^2 is a straight or branched carbon chain having from 2 to 10 carbons, n is from 1 to 10, and R^3 is selected from the group consisting of H, CH_3 , and CH_2CH_3 .
10. The aqueous ink jet ink of claim 8 wherein from 2 to 4 R groups are independently selected from the group consisting of sugars, polyols, and pyridiniums.



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EUROPEAN SEARCH REPORT

Application Number
EP 01 30 8438

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	US 5 542 972 A (RUSS WERNER H ET AL) 6 August 1996 (1996-08-06) * column 3, line 52,53; claims 1,2 *	1	C09D11/00
X	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 08, 30 June 1998 (1998-06-30) & JP 10 060344 A (KONICA CORP), 3 March 1998 (1998-03-03) * abstract *	1	
X	EP 0 769 531 A (KONISHIROKU PHOTO IND) 23 April 1997 (1997-04-23) * page 15, line 15-22 * * page 23, line 1-30; claim 1 *	1	
A	US 5 534 052 A (HASSEN RUECK KARIN ET AL) 9 July 1996 (1996-07-09) * column 3, line 20-24; claims 6,7 *	1	
A	US 4 360 589 A (KOJIMA TETSURO ET AL) 23 November 1982 (1982-11-23) * claim 1 *	7	
A	EP 0 641 669 A (AGFA GEVAERT NV) 8 March 1995 (1995-03-08) * page 5, line 28-58 *	7	C09D
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 14 November 2001	Examiner Von Kuzenko, M
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons S : member of the same patent family, corresponding document</p>			

EPO FORM 1503 05 82 (2/94/01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 01 30 8438

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

14-11-2001

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
US 5542972	A	06-08-1996	DE	4417718 A1	23-11-1995
			DE	59504248 D1	24-12-1998
			EP	0684292 A1	29-11-1995
			JP	8048897 A	20-02-1996

JP 10060344	A	03-03-1998	NONE		

EP 0769531	A	23-04-1997	JP	9111163 A	28-04-1997
			JP	9255887 A	30-09-1997
			EP	0769531 A1	23-04-1997
			US	5753017 A	19-05-1998

US 5534052	A	09-07-1996	DE	4341455 A1	08-06-1995
			DE	59407126 D1	26-11-1998
			EP	0657509 A1	14-06-1995
			JP	7196942 A	01-08-1995

US 4360589	A	23-11-1982	JP	1436062 C	25-04-1988
			JP	56159644 A	09-12-1981
			JP	62045545 B	28-09-1987
			DE	3119252 A1	11-03-1982
			GB	2077455 A ,B	16-12-1981

EP 0641669	A	08-03-1995	EP	0641669 A1	08-03-1995
			DE	69302401 D1	30-05-1996
			DE	69302403 D1	30-05-1996
			DE	69306778 D1	30-01-1997
			DE	69400350 D1	05-09-1996
			WO	9411198 A1	26-05-1994
			WO	9411199 A1	26-05-1994
			EP	0669875 A1	06-09-1995
			EP	0641670 A1	08-03-1995
			EP	0669876 A1	06-09-1995
			JP	7081053 A	28-03-1995
			JP	7081209 A	28-03-1995
			JP	8503175 T	09-04-1996
			JP	8504373 T	14-05-1996
			US	5621449 A	15-04-1997
			US	5568173 A	22-10-1996
			US	5587350 A	24-12-1996
			US	5536696 A	16-07-1996

EPO FORM P0439

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82